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On the comparison between equilibrium and disequilibrium condensation sequences of meteorites

BIBHAS R. DE

The Lunar Science Institute, 3303 NASA Road 1, Houston, Texas 77058

Abstract—We define a simple formalism for calculating the condensation sequence of meteoritic minerals in a cooling vapor phase in temperature disequilibrium (between the vapor phase and the condensed phase) when such minerals condense congruently. Certain preliminary comments are made about the possibility of judging the relative plausibility of the equilibrium and the disequilibrium models from the observations in meteorites if a monotonic cooling were indeed the course of condensation in either case.

INASMUCH AS ONE of the primary objectives of meteoritic research is to draw inferences about the physical conditions (primarily temperature and pressure) in the meteorite condensation environment, it is important to ask whether such condensation took place in a state of equilibrium between the vapor phase *kinetic* temperature T_k and the condensed phase *internal* temperature T_c. In physical models of the meteorite condensation environment, both equilibrium (see e.g., review by Anders, 1971, 1972) and disequilibrium (see e.g., Arrhenius, 1977 and earlier references) condensation processes are suggested. If the theoretical interpretation of the observations in meteorites is to shed some light on the relative plausibility of these suggestions, then the question arises as to how unambiguously we can translate the observations in meteorites to the physical conditions in the condensation environment.

One prevalent concept with regard to such theoretical interpretation is what has been referred to as a *condensation sequence* of the various meteoritic minerals. In the sense commonly discussed, this sequence is a theoretically determined temperature (and equivalently, time) sequence in which the various chemical species condense out in thermodynamic equilibrium as a vapor phase composed of a mixture of these species gradually cools from an initial high temperature (see e.g., reviews by Anders, 1971, 1972; Grossman, 1975). The composition and in some cases the texture of meteorites do not contradict such a time-temperature sequence. We should note in circumspection, however, that a condensation sequence may also arise from a gradual densification of the medium—or a combination of densification and cooling (see review by Arrhenius, 1977). Recent analysis of textural relations among different minerals (Wark and Lovering, 1977) actually indicates sequence reversals, possibly involving spatial or temporal changes in composition, temperature and density of the source medium.

In this paper, however, we assume the simple case of a time-temperature sequence to be the correct course of condensation. We then inquire from a physical point of view: If there were indeed a substantive evidence of a condensation sequence in the meteorites, does this fact by itself uniquely tell us that the condensation took place in thermodynamic equilibrium? If not, what information can we glean from the observed sequence? We shall try to explore these questions by examining how the condensation sequence behaves in the two limiting cases—those of complete equilibrium and extreme disequilibrium.

It should be noted that thermodynamic equilibrium implies chemical, mechanical, and thermal equilibria. In this paper we address ourselves only to the question of thermal equilibrium (temperature equilibrium). The validity of the other equilibrium assumptions should be examined separately.

At low pressures (≤ 1 torr), the equilibrium vapor pressure $P_0(T)$ of an element as a function of the temperature T is given by the empirical relation (see e.g., Dushman, 1958).

$$\log P_0(T) = A - B/T, \tag{1}$$

where A and B are known constants. Since this vapor pressure is dependent only on the condensed phase temperature, Eq. (1) may also be used for the vapor pressure in the case of temperature disequilibrium by replacing the common temperature T of the vapor and the condensed phases by the condensed phase temperature T_c.

Consider a cosmic gas phase dominated by molecular hydrogen of density N, which is assumed to be constant during the course of condensation. The abundance ratios f (by number) of the condensable substances relative to hydrogen are all negligible compared to unity. Then the temperature T_e of the onset of condensation of an element in the cooling vapor phase in equilibrium is given by the condition

$$\log (NfkT_e) = A - B/T_e, \tag{2}$$

where k is the Boltzmann constant. Clearly, the ordering of T_e for the various elements is the equilibrium condensation sequence for these elements.

It has long been suggested (Arrhenius and Alfvén, 1971; Arrhenius and De, 1973; De, 1973 and earlier references) that in a space environment, the relationship among the gas phase kinetic temperature T_k, the condensed phase internal temperature T_c, and the radiation field equivalent blackbody temperature T_0 (i.e., the temperature that a blackbody placed in the radiation field would attain in steady state) must in general be assumed to be one of disequilibrium. This relationship is determined by the thermal steady state requirement that the rate of heat loss by an entity of the condensed phase (a "grain") equal its rate of heat gain. For our purpose, we assume here the grains to behave as ideal blackbodies—an assumption which is not very realistic (see the discussion and analysis by De, 1977). However, it is unlikely that the effects which modify the blackbody behavior will alter the *sequence* of condensation temperatures of the various solids—and therefore we leave such effects out in the present discussion. Such effects will however influence the condensation temperatures themselves and should be included when more realistic estimates of these temperatures are desired. In the present case, the relationship among T_k, T_c, and T_0 is (*op. cit.*)

$$\sigma T_c^4 = \sigma T_0^4 + 2CNVk(T_k - T_c), \tag{3}$$

where σ = Stefan–Boltzmann constant, C = thermal accommodation coefficient for hydrogen molecules, and $V = (kT_k/2\pi m)^{1/2}$ is the effective impingement velocity of the hydrogen molecules onto the grain surface (m = mass of a hydrogen molecule). A state of extreme disequilibrium exists when the gas-grain medium is transparent in infrared radiation so that the radiation temperature T_0 is essentially determined by the neighboring star (*op. cit.*). A state of complete equilibrium exists when the medium is opaque to such radiation. The above equation allows us to calculate T_c as a function of T_k and hence the change in T_c as T_k is gradually lowered. The accommodation coefficient C appears from theoretical considerations to be independent or weakly dependent on T_k and T_c (McCarroll and Ehrlich, 1963; Kaminsky, 1965) and therefore we have assumed it to be a constant in our discussion.

The condition for *phase* equilibrium in the general state of temperature disequilibrium is that the rate of condensation (independent of T_c) equal the rate of evaporation (independent of T_k). These two rates are

$$R_{cond} = Nf\xi\left(\frac{kT_k}{2\pi m_c}\right)^{1/2}, \tag{4}$$

$$R_{ev} = N_{co}\left(\frac{kT_c}{2\pi m_c}\right)^{1/2}, \tag{5}$$

where ξ is the sticking probability of the condensable molecules in disequilibrium, m_c is the mass of a condensable molecule, and $N_{co} = P_0(T_c)/kT_c$ (i.e., N_{co} is the density of the condensables in a vapor phase in phase and temperature equilibrium with the condensed phase at the temperature T_c). For a given condensable substance, the disequilibrium condensation temperatures T_{cd} of the condensed phase and T_{kd} of the vapor phase are now found in the following way: Using Eq. (3), we calculate the change in T_c as T_k is gradually lowered. At the same time, we keep track of the rates R_{cond} and R_{ev}. When these two rates become equal, we set $T_{cd} = T_c$ and $T_{kd} = T_k$.

The parameter ξ is the major unknown in such a calculation. We have little knowledge about this parameter—but we expect it to be weakly dependent on T_k. This is so because we expect ξ to have a similar dependence on temperature as the corresponding thermal accommodation coefficient (since the higher the probability of accommodation, the higher is the probability of sticking), and the latter appears to be a weak function of T_k—as mentioned earlier. In any case, in our numerical illustration, we shall use values of ξ spanning over two orders of magnitude.

For the purpose of numerical illustration we have chosen a sample of 15 metallic elements whose condensation temperatures T_e and the thermochemical constants A and B cover a wide range. The resulting sequence is somewhat

1977LPSC....8...87D

fictitious as far as condensation of meteorites is concerned, since many of the chosen elements do not condense in the pure form. Nevertheless, this example may be used to illustrate certain features of disequilibrium condensation. We have somewhat arbitrarily chosen an initial vapor phase temperature $T_k = 3000°K$, and a gas density (density of hydrogen molecules) $N = 5 \cdot 10^{15}\ \mathrm{cm}^{-3}$ for both the equilibrium and the disequilibrium cases. The reason for choosing these numbers is to have a high gas temperature and yet retain hydrogen in molecular form and all elements in question in vapor phase. At the same time, when the gas cools down to ~2000°K, the gas temperature and pressure ($\sim 10^{-3}$ atm) are well within the range suggested in equilibrium models (see e.g., Anders, 1971). In any case, the above physical conditions are chosen purely for the purpose of illustrating the conclusions of this paper and are not meant to be suggestive otherwise. The temperature T_0 has been assumed to be 150°K (a typical value for the region between 2 and 4 a.u. from the sun, for instance; this region is often suggested to be the condensation environment of some meteoritic components). The abundance ratios f have been taken from Allen (1973), and the thermochemical constants A and B from Dushman (1958). The accommodation coefficient C has been set equal to unity, giving an upper limit to T_c for a given T_k. The resulting equilibrium and disequilibrium sequences are presented in Table 1.

A number of points are to be noted from Table 1: (a) the sequence of condensation temperatures remains unchanged in spite of large degrees of disequilibrium and large changes in ξ; (b) the disequilibrium condensation temperatures T_{cd} are dependent on ξ and are in general lower than the equili-

Table 1. Condensation temperatures (in degrees Kelvin) in complete equilibrium and extreme disequilibrium.

		T_{cd}, T_{kd}		
Element	T_e	$\xi = 1.0$	0.1	0.01
Fe	1411	1416,2941	1316,2615	1229,2360
Ni	1353	1355,2737	1271,2480	1196,2270
Al	1051	1038,1890	968,1747	906,1631
Cu	1027	1015,1841	957,1725	905,1629
Au	908	894,1610	849,1534	809,1470
Ge	871	852,1539	802,1460	758,1395
Ga	750	725,1349	684,1296	648,1251
Sn	732	707,1325	667,1275	632,1232
Ag	710	687,1300	654,1259	624,1223
In	639	611,1208	579,1172	550,1142
Ca	625	588,1182	547,1139	512,1103
Mg	555	513,1104	477,1069	446,1040
Pb	519	487,1079	461,1054	438,1033
Bi	490	460,1053	437,1032	417,1014
Tl	433	403,1002	384,985	366,970

brium condensation temperatures; (c) with change in ξ, T_{cd} for various elements changes by varying amounts, but not in such a way as to mar the sequence down to $\xi = 10^{-2}$, and (d) if ξ were close to unity, then T_e and T_{cd} would not be drastically different.

The conclusion (a) above is not surprising, since the condensation sequence for the various elements depends on their respective vaporization energies—and thus is not dependent on the equilibrium or disequilibrium assumption. The same is true for chemical compounds that undergo congruent condensation and evaporation (i.e., the substances have the same chemical composition in the vapor phase as in the condensed phase; in this case, however, Eq. (1) should be replaced by its appropriate counterpart for the compounds—see e.g., Grossman, 1972 and references therein). The only exception to this rule occurs when the vapor pressure curves in the pressure-temperature plane of two substances X and Y (elements or compounds) intersect each other within the pressure-temperature regime of interest. In this case, a sequence reversal of X and Y in the disequilibrium case occurs if the equilibrium condensation temperatures T_e and the disequilibrium condensation temperatures T_{cd} lie on opposite sides of the point of intersection. For pure elements, such intersections are very rare in the pressure-temperature regime of interest in either equilibrium or disequilibrium theories (see e.g., vapor pressure diagrams of Honig, 1962). In the case of compounds that condense congruently in the equilibrium theories, examples of some such intersections are found in the diagram of Barshay and Lewis (see Fig. 1 in Barshay and Lewis, 1976). If the equilibrium and the disequilibrium sequences for the compounds were to be calculated for the same temperature range and the same density as we have done above for the elements, and if the observed sequence occurred in the high-temperature segment, then such intersections would put upper limits on the permissible degree of disequilibrium—since in this case T_{cd}'s and T_e's for any pair of "intersecting compounds" must lie on the same side of the point of intersection. Aside from such possible limiting constraints, equilibrium and disequilibrium models would predict the same condensation sequence—although starting from widely different physical conditions (the disequilibrium model suggesting much higher gas temperatures and much lower gas densities than the equilibrium models). On the basis of our discussion thus far, we are then forced to conclude that an observed "equilibrium sequence" cannot shed any light on the relative merits of the equilibrium and the disequilibrium suggestions (nor on the condensed phase condensation temperatures).

There are, however, three important effects which can give rise to disagreements in the equilibrium and disequilibrium sequences. First, if the parameter ξ is drastically different from one substance to another so that the conclusion (c) reached in the preceding is no longer valid, then the condensation sequences will disagree. Secondly, if the disequilibrium gas temperature T_k is so high that the effects of ionization and dissociation come into play, then again the sequences will disagree. Some such disagreements have been discussed by Arrhenius and Alfvén (1971). Lastly, even in absence of ionization and dissociation, the gas phase-condensed phase chemical reaction history may differ in the equilibrium and the disequilibrium cases. Such history in the case of equilibrium has been traced in detail by Grossman (1972, 1975). No such study has been done for the case of disequilibrium. Arrhenius (1977), however, points out that the observations that seem to lend credence to Grossman's chemical history may also be rationalized on the basis of disequilibrium condensation. In fact, it appears (*op. cit.*) that certain observations are better understood if the condensed phase condensation temperatures were lower than the equilibrium condensation temperatures. Such a condition is realizable in disequilibrium (see e.g., Table 1)—especially when gas densities much lower than those in the equilibrium suggestion are considered.

The true relationship between T_k and T_c in the meteorite condensation environment probably lies somewhere between complete equilibrium and extreme disequilibrium. In order to make further progress in this area based on observations in meteorites, it is necessary to sort out those specific observations that are sensitive to the $T_k - T_c$ relationship. We hope that this brief note may serve to put some of the relevant physical considerations in this regard in better perspective.

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1977LPSC....8...87D

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